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1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE Technical Papers	3. DATES COVERED (From - To)

4. TITLE AND SUBTITLE

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

5d. PROJECT NUMBER
2303

5e. TASK NUMBER
M2C8

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/PRS
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8. PERFORMING ORGANIZATION REPORT

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Leilani Richardson
a. REPORT Unclassified	**b. ABSTRACT** Unclassified	**c. THIS PAGE** Unclassified	A		19b. TELEPHONE NUMBER (include area code) (661) 275-5015

1122 031

MEMORANDUM FOR IN-HOUSE PUBLICATIONS

FROM: PROI (TI) (STINFO)   23 Nov 98

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-TP-FY99-0028
Presilla-Marquez, Carrick, Larson, "Vibrational spectra of linear BC_3 and linear B_2C_2 in argon at 10 K"
                    Journal submission   (Statement A)

Vibrational spectra of linear BC_3 and linear B_2C_2 in argon at 10 K[a]

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Submitted: May 20, 1997
Revised: November 16, 1998

20021122 031

(a) Presented in part at the 52nd Ohio State University International Symposium on Molecular Spectroscopy, Columbus, Ohio, June 16-20, 1997.
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ABSTRACT

The vibrational spectra of linear BC_3 and linear B_2C_2 in an argon matrix at ~~ten degrees Kelvin~~ 10 K have been observed for the first time by Fourier transform infrared spectroscopy. Mixtures of boron and carbon powders were vaporized in a resistively heated (~ 3000 K) oven. BC_3 was produced during co-deposition of the vapors with argon onto a CsI substrate maintained at 10 K; B_2C_2 was observed only after annealing the matrices. Frequencies measured at 2002.1 and 1512.5 cm^{-1} have been assigned to the $\nu_1(\sigma)$ and $\nu_2(\sigma)$ B-C stretching fundamentals of linear BC_3 and a frequency measured at 955.0 cm^{-1} has been assigned to the $\nu_3(\sigma_u)$ stretching fundamental of linear symmetric BC_2B. These assignments are based on FTIR measurements of the majority of the BC_3 and B_2C_2 isotopomer frequencies and are consistent with the results from Rittby's collaborative ab-initio study.

I. INTRODUCTION

The Propulsion Directorate of the U.S. Air Force Research Laboratory has supported research and development of high energy density materials (HEDM) for more than a decade.[1-3] One direction of basic research has involved trapping atoms and small clusters in suitable cryogenic substrates. Trapped clusters have been identified by comparison of their experimental infrared spectrum to the predictions of *ab initio* calculations. This allows calculation of their ground state potentials, which enables quantification of the heat of formation of multicomponent HEDM and thereby its potential performance as a rocket propellant. Additionally, annealing studies of the HEDM matrices provide information about the stability of these potentially high performance propellants.

Previously[4], we reported experimental conditions for production of BC_2 in an argon matrix at 10 K, using a resistively heated (3000 K) oven to generate mixtures of boron/carbon vapors. A vibration at 1194.4 cm^{-1} was assigned to the ν_2 fundamental of cyclic, "effectively" symmetric BC_2, on the basis of a complete set of measured isotopic shifts. In this paper we report findings on BC_3 and B_2C_2, which were observed in the same matrices where BC_2 was previously identified. BC_3 and BC_2 were produced in the originally deposited matrix and gradually decreased during multiple annealings above 25 K. However, B_2C_2 was formed only after annealing the condensate. Measured isotopomer frequencies were compared to Rittby's *ab-initio* predictions[5] to identify these two new molecules.

II. EXPERIMENTAL PROCEDURE

Mixtures of boron and carbon powders, in various ratios and isotopic compositions, were heated in tantalum cells with graphite liners to temperatures as high as 3000 K. The cells were packed with about 0.2 g of material, consisting of approximately equal amounts of the powder mixture and the solid cylindrical graphite liner. Boron and carbon vapors escaped through a 0.1 cm diameter hole and condensed with argon onto a CsI substrate maintained at 10 K. Over the course of one-hour, a matrix of about 60 μm thickness was produced. Details about preparation of matrix samples, annealing of matrices and recording spectra were described in the previous paper;[4] additional details and methods have been described in our papers[6,7] on identification of cyclic and linear carbon clusters.

III. RESULTS AND DISCUSSION

(i) Vibrational spectrum of BC_3.

Figure 1(a)-(e) shows the spectra of matrices with B/C ~ 1/3 to ~ 1/8 and isotopic compositions as follows: matrix (a) natural abundance carbon (^{12}C = 99%, ^{13}C = 1%) and natural abundance boron (^{11}B = 80.22%, ^{10}B = 19.78%); matrix (b) natural abundance carbon and boron enriched with boron-10 (^{11}B = 27.1%, ^{10}B = 72.9%); matrix (c) natural abundance boron and carbon slightly enriched with carbon-13 (^{12}C ≈ 80%, ^{13}C ≈ 20%); matrix (d) boron heavily enriched with boron-10 (^{11}B ≈ 10%, ^{10}B ≈ 90%) and carbon slightly enriched with carbon-13 (^{12}C = 89%, ^{13}C = 11%); and matrix (e) natural abundance boron and carbon heavily enriched with carbon-13 (^{12}C = 27%, ^{13}C = 73%).

Fig. 1(a) shows an absorption at 1543.1 cm⁻¹, identified[8] here as the $v_3(\sigma_u)$ mode of linear C_4, and two unidentified absorptions at 1512.5 and 1530.0 cm⁻¹, which were absent when only

carbon was evaporated. These two bands maintained a constant intensity ratio of ~ 4:1, both throughout the annealing experiments, where they decreased by a factor of about two, and when different boron/carbon ratios or evaporation/deposition temperatures were used. This correlation strongly suggests that these two bands originate from a single B_xC_y cluster.

Figure 1(b) shows the spectrum produced by matrix (b), which was enriched with boron-10, $^{11}B:^{10}B = 1:2.7$. If the 1512.5 and 1530.0 cm^{-1} bands in Fig. 1(a) originated from two different vibrational modes of a single B_xC_y cluster, then two new bands, shifted to higher frequency, would have been observed in the same 4:1 intensity ratio shown by Fig. 1(a). However, Fig 1(b) shows that the bands do not shift; rather the first is suppressed and the second is amplified, and their intensity ratio reverses from ≈ 4:1 in Fig. 1(a) to ≈ 1:3 in Fig. 1(b), which are approximately the $^{11}B:^{10}B$ isotopic ratios of the matrices. Moreover, since a single boron isotopic shift is observed, the cluster in question contains only one boron atom, which identifies $^{11}B^{12}C_x$ at 1512.5 cm^{-1} and $^{10}B^{12}C_x$ at 1530.0 cm^{-1}. The number of carbons in this molecule may be deduced by analysis of spectra obtained from carbon-13 enriched matrices.

Figures 1(c) to 1(e) show spectra obtained from matrices enriched with carbon-13. The bands belonging to isotopomers of the $v_3(\sigma_u)$ mode of linear C_4 are seen throughout the spectra. To distinguish these from bands belonging to carbon-13 isotopomers of BC_x, the isotopomer bands of C_4 from this work and the literature[8] have been summarized in Table I and compared with theoretical results of Rittby[9]. Figure 1(e) was obtained from a matrix heavily enriched with carbon-13 and clearly shows a band at 1483.4 cm^{-1}, which we assign as the $v_3(\sigma_u)$ mode of the fully substituted $^{13}C_4$ isotopomer. This band, reported here for the first time, is also in good agreement with the theoretical prediction.[9] Also, three of the doubly substituted C_4 isotopomers,

BC$_3$ isotopomers (at 1500.1, 1497.0 and 1494.3 cm^{-1}) increases with the square of the ^{13}C/^{12}C ratio. Thus, the ability to differentiate the three ^{11}B^{13}C^{12}C$_2$ bands from the two interfering ^{13}C$_3$^{12}C bands was optimized in matrix (c) by use of a relatively low carbon-13 enrichment around 20%.

Matrix (d) was enriched with somewhat less carbon-13 than matrix (c) [^{12}C/^{13}C = 8/1] but was heavily enriched with boron-10 to enhance the yields of the singly substituted ^{10}BC$_3$ isotopomers of carbon-13. Fig. 1(d) shows that the ^{10}BC$_3$ band at 1530.0 cm^{-1} is now larger than the bands of the two singly substituted ^{13}C^{12}C$_3$ isotopomers. Two well-defined new bands appear at 1516.5 and 1515.0 cm^{-1}, on the high-frequency side of the interfering doubly substituted ^{13}C$_2$^{12}C$_2$ isotopomer bands. Their absorbances are each about 1/8 the absorbance of the ^{10}BC$_3$ band at 1530.0 cm^{-1}, which is consistent with the carbon-13 enrichment of this matrix and their belonging to two singly substituted ^{10}B^{13}C^{12}C$_2$ isotopomers. The third band appears at 1513.3 cm^{-1} and is assigned to the third ^{10}B^{13}C^{12}C$_2$ isotopomer; the absorbance of this band is slightly larger than the other two bands due to a small contribution from three of the four doubly substituted ^{13}C$_2$^{12}C$_2$ isotopomers at 1513.6 cm^{-1}. In this spectral region the yield of interfering doubly substituted ^{13}C$_2$^{12}C$_2$ isotopomers relative to the yield of the singly substituted ^{10}B^{13}C^{12}C$_2$ isotopomers increases with the first power of the ^{13}C/^{12}C ratio. Thus, in matrix (d), the relatively low enrichment of 11% carbon-13 combined with a high enrichment of 90% boron-10 was about optimum to minimize interference.

In matrix (e) natural abundance boron was mixed with highly enriched carbon-13, ^{12}C/^{13}C = 1/2.7. One clearly defined new band appeared in its spectrum at 1467.9 cm^{-1} with signal to noise ratio (S/N) ~ 2. This band was assigned to the fully substituted ^{11}B^{13}C$_3$, which is expected to be the dominant BC$_3$ cluster in this matrix and to show the observed nominal red shift from the ^{13}C$_4$ band. The yields of each of the three doubly substituted ^{11}B^{13}C$_2$^{12}C isotopomers are

Over the frequency range 1980 to 2030 cm^{-1}, where the $v_1(\sigma)$ fundamental is expected, numerous bands attributable to species that contain boron and carbon are observed. In the absence of boron, the only bands that appear in this region belong to linear C_9 at 1997.8 cm^{-1} (Refs. 10,11) and the singly substituted isotopomers of linear C_3, 12-12-13 at 2026.1 and 12-13-12 at 1987.5 cm^{-1} (Ref. 12). The spectra from matrix (b) [$^{11}B/^{10}B = 1/2.7$] show a pair of bands at 2002.1 and 2006.8 cm^{-1} with about 25% the absorbance of the $v_2(\sigma)$ bands. They maintain a constant intensity ratio $\sim 1/3$ while decreasing by a factor of about two over the course of four annealings, closely coupled to the $v_2(\sigma)$ bands. Other than the C_3 isotopomer band at 1987.5 cm^{-1}, these two bands are the only ones in this frequency range that decrease during annealing.

In matrix (a) an unidentified peak at 2008.2 cm^{-1} obscures the 2006.8 cm^{-1} band. The band at 2002.1 cm^{-1}, on the low frequency side of an unidentified band at 2003.6 cm^{-1}, has about 25% the absorbance of the $v_2(\sigma)$ band. It decreases by a factor of two during annealing while correlating with the decrease in the $v_2(\sigma)$ band, similar to its behavior in matrix (b). If the 2002.1 cm^{-1} band were assigned to the $v_1(\sigma)$ mode of $^{11}BC_3$, then the scale factor[5] is $S_F = 2002.1/2066.3$ = 0.96093, very close to the scale factor calculated for the $v_2(\sigma)$ mode, 0.97250. The scaled theoretical boron isotope shift is 4.9 cm^{-1}, which is in excellent accord with the measured isotopic shift of 4.7 cm^{-1}. The absorbance is about 25% of that of the $v_2(\sigma)$ fundamental, which compares favorably with the 16% figure predicted by theory. These findings enable tentative assignment of the 2002.1 cm^{-1} band to the $v_1(\sigma)$ fundamental of BC_3. Spectra of the carbon-13 enriched matrices were too congested in this spectral region to provide evidence for a conclusive assignment.

Burkholder and Andrews[13] assigned bands at 2002.5 and 2007.2 cm^{-1} in an argon matrix to ^{11}BCO and ^{10}BCO molecules, which were produced by co-condensing laser ablated boron with

dilute CO in argon. However, we rule out the possibility that the 2002.1 and 2006.8 bands belong to [11]BCO and [10]BCO, which may otherwise originate from boron atom reaction with CO impurity, because the ubiquitous CO contamination found in all matrix isolation work was minimal in these experiments. Further, the absorption by CO appears in our matrices at 2138.0 cm^{-1}, which is identical to the CO absorption frequency reported by Burkholder and Andrews. Thus, although the boron isotope shift for the BCO mode reported by these authors is the same as that for the $\nu_1(\sigma)$ mode of BC_3 reported here, the very small 0.4 cm^{-1} difference between their frequencies is significant and rules out the 2002.1 cm^{-1} band as belonging to [11]BCO.

(ii) Vibrational spectrum of B_2C_2.

Figure 3 shows the spectra of the same matrices displayed in Fig. 1 over the frequency range 930 - 985 cm^{-1} after one annealing at 27.5 K for 150 s. All of the bands in Fig. 3 were produced only after annealing matrices containing both boron and carbon. During additional annealings all the bands maintained constant absorbance ratios, which is consistent with their all belonging to isotopomers of the same molecule.

Figure 3(a) shows three approximately equally spaced bands at 955.0, 967.7 and 979.0 cm^{-1} whose absorbances correlated in a ratio of 16:8:1 after sequential annealings to higher temperatures. The observed 16:8:1 ratio and the nearly equal spacing of bands (12.7 and 11.3 cm^{-1}) is the signature of a molecule formed from natural abundance boron ($^{11}B/^{10}B = 4/1$) that contains two equivalent boron atoms. The spectrum of matrix (b), in which $^{11}B/^{10}B \sim 1/3$, shows the same pattern, but with the absorbance ratios inverted to 1:5.4:7.3. Therefore the three bands originate from a single vibrational mode of three isotopomers of B_2C_x and their assignments are $^{11}B_2C_x$ at 955.0, $^{10,11}B_2C_x$ at 967.7 and $^{10}B_2C_x$ at 979.0 cm^{-1}.

Don't split

Two triplets have the $^{10}B_2^{13}C_2$ isotopomer in common: $^{11}B_2^{13}C_2$, $^{10,11}B_2^{13}C_2$, $^{10}B_2^{13}C_2$ and $^{10}B_2^{12}C_2$, $^{10}B_2^{12,13}C_2$, $^{10}B_2^{13}C_2$. In Fig. 3(e) the band at 950.6 cm^{-1} was assigned to the $^{10,11}B_2^{13}C_2$ isotopomer. The expected absorbance ratio with $^{11}B/^{10}B = 4/1$ is $[^{11}B_2^{13}C_2]$: $[^{10,11}B_2^{13}C_2]$: $[^{10}B_2^{13}C_2] = 16 : 8 : 1$, which is consistent with the observed $[^{11}B_2^{13}C_2]$: $[^{10,11}B_2^{13}C_2]$ ~ 2 : 1 and the lack of signal from $^{10}B_2^{13}C_2$ in Fig. 3(e).

In Fig. 3(d) the band at 970.2 cm^{-1} was assigned to the $^{10}B_2^{12,13}C_2$ isotopomer. The expected absorbance ratio with $^{12}C/^{13}C$ ~ 9/1 is $[^{10}B_2^{12}C_2]$: $[^{10}B_2^{12,13}C_2]$: $[^{10}B_2^{13}C_2] = 81 : 18 : 1$, which is consistent with the observed $[^{10}B_2^{12}C_2]$: $[^{10}B_2^{12,13}C_2]$ ~ 5 : 1 and the lack of signal from $^{10}B_2^{13}C_2$. Also, the $^{10,11}B_2^{12}C_2$ isotopomer at 967.7 cm^{-1} appears in this spectrum with absorbance about equal to the $^{10}B_2^{12,13}C_2$ isotopomer, which is consistent with the expectation for matrix (d), viz., $[^{10,11}B_2^{12}C_2]$: $[^{10}B_2^{12,13}C_2] = [^{11}B/^{10}B] [^{12}C/^{13}C]$ ~ (1/9)(9/1).

No band attributable to $^{10,11}B_2^{12,13}C_2$ isotopomers appears in any of the matrices. If the geometry of B_2C_2 were of high symmetry, e.g., a rhombus with four B-C bonds, only one $^{10,11}B_2^{12,13}C_2$ isotopomer band is possible. In this case the expected absorbance ratio in the spectrum of matrix (e), $[^{10,11}B_2^{12,13}C_2]_{rhombic}$: $[^{10,11}B_2^{13}C_2]_{rhombic} = 2 [^{12}C/^{13}C]_{matrix (e)}$ ~ 4/2 (1/2.7) ~ 0.74 : 1, where the factor of 4/2 is the statistical weight ratio for the rhombic isotopomers. Since the $^{10,11}B_2^{13}C_2$ band is clearly discernable with S/N > 2 in Fig 3(e) and there is no other nearby blue-shifted band attributable to the $^{10,11}B_2^{12,13}C_2$ isotopomer, the rhombic geometry for B_2C_2 may be ruled out. If the B_2C_2 geometry contains B-B and/or C-C bonds, (e.g., linear or trapezoidal geometries), then two distinguishable forms of the $^{10,11}B_2^{12,13}C_2$ isotopomer are possible. In this case, the expected absorbance ratio in the spectrum of matrix (e) is $[^{10,11}B_2^{12,13}C_2]_{linear,trapezoid}$: $[^{10,11}B_2^{13}C_2]_{linear,trapezoid} = 2/2 [^{12}C/^{13}C]_{matrix (e)}$ ~ 2/2 (1/2.7) ~ 0.37 : 1, so that the two $^{10,11}B_2^{12,13}C_2$ isotopomer bands would be lost in the baseline noise of the spectrum in Fig 3(e). Similar analysis

Figure 4 compares the experimental measurements to theoretical distributions of isotopomer frequencies for the modes considered above. All the modes shown [except $\nu_5(b_2)$ of the trapezoid] have similar form and are dominated by the same internal coordinate motion, namely B-C stretching[5]. The magnitudes of the projections of the atomic displacements along the B-C bonds for the $\nu_3(b_{1u})$ and $\nu_4(b_{2u})$ modes of the rhomboidal isomer and the $\nu_2(a_1)$ mode of the trapezoidal isomer are very similar to the displacements in the $\nu_3(\sigma_u)$ mode of both linear isomers[5]. Although Fig. 3 shows that the theoretical frequency pattern for isotopomers of linear BCCB is the best match to the experimental pattern, it is very similar overall to those of the other geometries. Not all isotopomers have the same ability to discriminate among geometries. Thus, the differences between theory and experiment are minimal for isotopomers with only two different isotopes ($^{10}B_2^{12}C_2$, $^{10}B_2^{13}C_2$, $^{11}B_2^{12}C_2$, $^{11}B_2^{13}C_2$) and they significantly larger for isotopomers with three or four different isotopes. Table VI compares the experimental isotopomer frequencies to scaled theoretical frequencies of the $\nu_3(\sigma_u)$ mode of linear BCCB. Differences between theory and experiment are small. However, while this good agreement between experimental and calculated isotopomer patterns is necessary to establish a theoretical geometry, it is not sufficient. In this case the excellent scale factor for the 955.0 cm^{-1} band is compelling evidence that enables conclusive assignment of this band to the $\nu_3(\sigma_u)$ mode of linear BCCB.

IV. CONCLUSIONS

As the result of collaborative studies involving *ab initio* calculations[5] and Fourier transform infrared matrix measurements, the BC$_3$ and B$_2$C$_2$ molecules have been identified for the first time. Frequencies at 2002.1 and 1512.5 cm^{-1} have been assigned to the $\nu_1(\sigma)$ and $\nu_2(\sigma)$

B-C stretching fundamentals of linear BC_3. A frequency at 955.0 cm^{-1} has been assigned to the $\nu_3(\sigma_u)$ B-C stretching fundamental of linear symmetric BCCB. For BC_3, the experimental data included measurement of nine of the sixteen[16] possible isotopomer frequencies of the $\nu_2(\sigma)$ mode, and two of the sixteen[16] possible frequencies of the $\nu_1(\sigma)$ mode. For B_2C_2, seven of the ten[10] possible isotopomer frequencies of the $\nu_2(\sigma_u)$ mode were measured. The measurements are in excellent agreement with the *ab initio* predictions. Also, the absorption by the $\nu_3(\sigma_u)$ mode of linear $^{13}C_4$ was measured at 1483.4 cm^{-1}, apparently for the first time.

ACKNOWLEDGMENTS

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FIGURE CAPTIONS

Fig. 1. FTIR spectra of the $\nu_2(\sigma)$ mode of isotopomers of linear BC_3 and the $\nu_3(\sigma_u)$ mode of isotopomers of linear C_4. The spectra were recorded at 10K after annealing the matrices with the indicated compositions at 27.5 K for 150 s. The large open triangles at the bottom show the predicted frequencies of linear BC_3 isotopomers (as explained in the text) and small filled triangles show measured isotopomer frequencies.

Fig. 2. Spectra obtained from matrix (a) $[^{11}B/^{10}B = 4/1]$ and matrix (b) $[^{11}B/^{10}B = 1/2.7]$ showing correlation upon annealing of the $\nu_1(\sigma)$ bands of $^{10}BC_3$ and $^{11}BC_3$ at 2006.8 and 2002.1 cm^{-1} with the $\nu_2(\sigma)$ bands at 1530.0 and 1512.5 cm^{-1}. The spectra labeled "0" are from the originally deposited matrix. Labels "1" to "4" indicate spectra recorded after the first through fourth annealing as follows: (1) 27.5 K for 150 s, (2) 30.0 K for 75 s, (3) 32.5 K for 45 s, (4) 35.0 K for 30 s. Frequency and absorbance scales are identical for all spectra. To facilitate comparisons between matrices, the matrix (b) spectra are multiplied by 1.4.

Fig. 3. FTIR spectra of the $\nu_3(\sigma_u)$ mode of isotopomers of linear BCCB. The spectra were recorded after annealing the matrices with the indicated compositions at 27.5 K for 150 s. The large open triangles at the bottom show the predicted frequencies of linear BCCB isotopomers (as explained in the text) and small filled triangles show measured isotopomer frequencies.

Fig. 4. Comparison of experimental isotopomer frequencies to scaled theoretical isotopomer frequencies for the most intense modes of four B_2C_2 geometries as calculated by Rittby, Ref. 5.

Table I. The $\nu_3(\sigma_u)$ mode of linear C_4 ($^3\Sigma_u^-$). Comparison of experimental frequencies (cm^{-1}) in argon at 10 K to predicted isotopomer frequencies [DFT/BVWN5/6-31G*] as calculated by Rittby, Ref. 9.

Isotopomer (w)[a]	Predicted frequency[b]	Experimental frequency	
		Literature[c]	This work
12-12-12-12 (1)	1543.1	1543.4	1543.1
13-12-12-12 (2)	1528.3	1528.8	1528.6
12-13-12-12 (2)	1527.0	1527.5	1527.2
13-12-13-12 (2)	1513.1	1513.8	1513.6
12-13-13-12 (1)	1513.0	1513.8	1513.6
13-12-12-13 (1)	1513.0		1513.6
12-12-13-13 (2)	1510.9	1511.6	1511.5
12-13-13-13 (2)	1497.9	1498.8	1498.6
13-12-13-13 (2)	1496.6	1497.7	1497.6
13-13-13-13 (1)	1482.5		1483.4

[a]Statistical weights (w) indicated in parenthesis.
[b]Predicted frequency = S_F x calculated frequency, with scale factor $S_F = 1.0095$ = observed frequency/calculated frequency.
[c]Ref. 8.

Table II. Theoretical harmonic frequencies (cm^{-1}) and intensities (km mol^{-1}) of linear BC$_3$ ($^4\Sigma$), [DFT/B3LYP/6-311G(2d)] as calculated by Rittby, Ref. 5.

mode	Frequency	Intensity
$\nu_1(\sigma)$	2066	24
$\nu_2(\sigma)$	1552	153
$\nu_3(\sigma)$	937	1.2
$\nu_4(\pi)$	437	9.8
$\nu_5(\pi)$	191	2.3

Table III. The $\nu_2(\sigma)$ fundamental vibration of linear BC_3. Comparison of observed frequencies to theoretical isotopomer frequencies (cm^{-1}) [DFT/B3LYP/6-311G(2d)] as calculated by Rittby, Ref. 5.

Isotopomer	Frequency $\nu_2(\sigma)$		
B-C-C-C	Scaled Theoretical[a]	Observed	Difference[b]
11-12-12-12	1512.5	1512.5	
11-13-12-12	1494.6	1494.3	+0.3
11-12-13-12	1499.4	1500.1	-0.7
11-12-12-13	1496.8	1497.0	-0.2
11-13-13-12	1483.6		
11-13-12-13	1479.9		
11-12-13-13	1482.5		
11-13-13-13	1467.7	1467.9	+0.2
10-12-12-12	1530.6	1530.0	+0.6
10-13-12-12	1514.3	1513.3	+1.0
10-12-13-12	1516.5	1516.5	0
10-12-12-13	1515.5	1515.0	+0.5
10-13-13-12	1502.2		
10-13-12-13	1500.0		
10-12-13-13	1500.0		
10-13-13-13	1486.8		

[a]Scale factor = 0.97455 = 1512.5 (observed)/1552.0 (theoretical).

[b]Difference = ν(scaled theoretical) - ν(observed).

Table IV. Experimental B_2C_2 isotopomer frequency patterns. Frequencies and frequency intervals (cm^{-1}) in three-band triplets of B_2C_2 isotopomers.

Boron isotope triplets				Carbon isotope triplets			
isotopomer	freq	intervals		isotopomer	freq	intervals	
		short	long			short	long
$^{10}B_2{}^{12}C_2$	979.0			$^{10}B_2{}^{12}C_2$	979.0		
		11.3				8.8	
$^{10,11}B_2{}^{12}C_2$	967.7		24.0	$^{10}B_2{}^{12,13}C_2$	970.2		(16.7)[a]
		12.7				(7.9)[a]	
$^{11}B_2{}^{12}C_2$	955.0			$^{10}B_2{}^{13}C_2$	(962.3)[a]		
$^{10}B_2{}^{12,13}C_2$	970.2			$^{10,11}B_2{}^{12}C_2$	967.7		
		(11.5)[a]				(9.0)[a]	
$^{10,11}B_2{}^{12,13}C_2$	(958.7)[a]		24.4	$^{10,11}B_2{}^{12,13}C_2$	(958.7)[a]		17.1
		(12.9)[a]				(8.1)[a]	
$^{11}B_2{}^{12,13}C_2$	945.8			$^{10,11}B_2{}^{13}C_2$	950.6		
$^{10}B_2{}^{13}C_2$	(962.3)[a]			$^{11}B_2{}^{12}C_2$	955.0		
		(11.7)[a]				9.2	
$^{10,11}B_2{}^{13}C_2$	950.6		(24.8)[a]	$^{11}B_2{}^{12,13}C_2$	945.8		17.5
		13.1				8.3	
$^{11}B_2{}^{13}C_2$	937.5			$^{11}B_2{}^{13}C_2$	937.5		

[a]Frequencies and intervals in parenthesis were interpolated or extrapolated from measured quantities.

Table V. Theoretical frequencies (cm^{-1}) and intensities (km mol^{-1}) of normal modes of minimum energy geometries of $^{11}B_2{}^{12}C_2$ as calculated by Rittby, Ref. 5.

Linear BCCB $(^1\Sigma_g)$ DFT/3BLYP/6-311G(2d) B-C = 1.561 Å C-C = 1.233 Å		Linear CBBC $(^1\Sigma_g)$ DFT/B3LYP/6-31G* B-C = 1.464 Å B-B = 1.503 Å		Rhombic CBCB (^1A_g) DFT/B3LYP/6-31G* B-C = 1.509 Å ∠B-C-B = 110.1°		Trapezoidal CCBB $(^1A_1)$ DFT/B3LYP/6-31G* B-C = 1.549 Å C-C = 1.335 Å B-B = 1.729 Å	
mode	freq	intens					
			mode	freq	intens		
					mode	freq	intens
						mode	freq	intens
$\nu_1(\sigma_g)$ 2206		$\nu_1(\sigma_g)$ 1779		$\nu_1(a_g)$ 1167		$\nu_1(a_1)$ 1421	83
$\nu_2(\sigma_g)$ 712		$\nu_2(\sigma_g)$ 692		$\nu_2(a_g)$ 544		$\nu_2(a_1)$ 1048	29
$\nu_3(\sigma_u)$ 982	1004	$\nu_3(\sigma_u)$ 1297	535	$\nu_3(b_{1u})$ 773	435	$\nu_3(a_1)$ 647	93
$\nu_4(\pi_g)$ 78		$\nu_4(\pi_g)$ 212		$\nu_4(b_{2u})$ 687	113	$\nu_4(a_2)$ 442	
$\nu_5(\pi_u)$ 65	34	$\nu_5(\pi_u)$ 100	21	$\nu_5(b_{3g})$ 1184		$\nu_5(b_2)$ 727	180
				$\nu_6(b_{3u})$ 447	6.8	$\nu_6(b_2)$ 402	7.6

Table VI. The $\nu_3(\sigma_u)$ fundamental vibration of linear BCCB. Comparison of observed frequencies to theoretical isotopomer frequencies (cm^{-1}) [DFT/B3LYP/6-311G(2d)] as calculated by Rittby, Ref. 5.

Isotopomer	Frequency $\nu_3(\sigma_u)$		
B-C-C-B	Scaled Theoretical[a]	Observed	Difference[b]
11-12-12-11	955.0	955.0	
11-12-13-11	945.8	945.8	0.0
11-13-13-11	937.2	937.5	-0.3
10-12-12-10	979.4	979.0	0.4
10-12-13-10	970.4	970.2	0.2
10-13-13-10	962.1	(962.3)[c]	(-0.2)
11-12-12-10	967.9	967.7	0.2
11-12-13-10	959.1	(958.7)	(0.4)
11-13-12-10	958.5	(958.7)	(-0.2)
11-13-13-10	950.4	950.6	-0.2

[a]Scale factor = 0.972515 = 955.0 (observed)/982.0 (theoretical)

[b]Difference = ν(scaled theoretical) - ν(observed).

[c]Extrapolated/interpolated quantities based on analysis of triplet intervals, see text and Table IV.
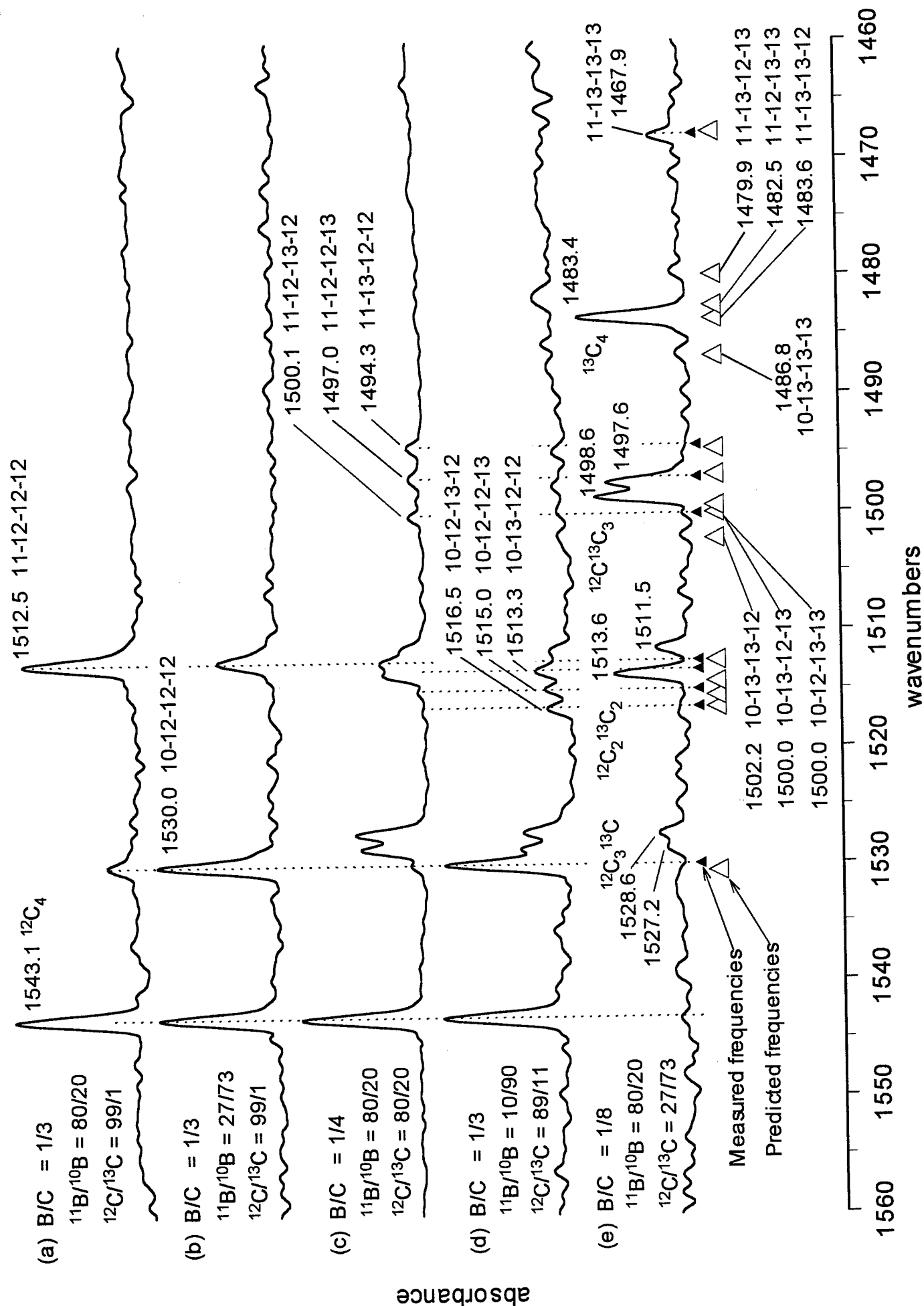
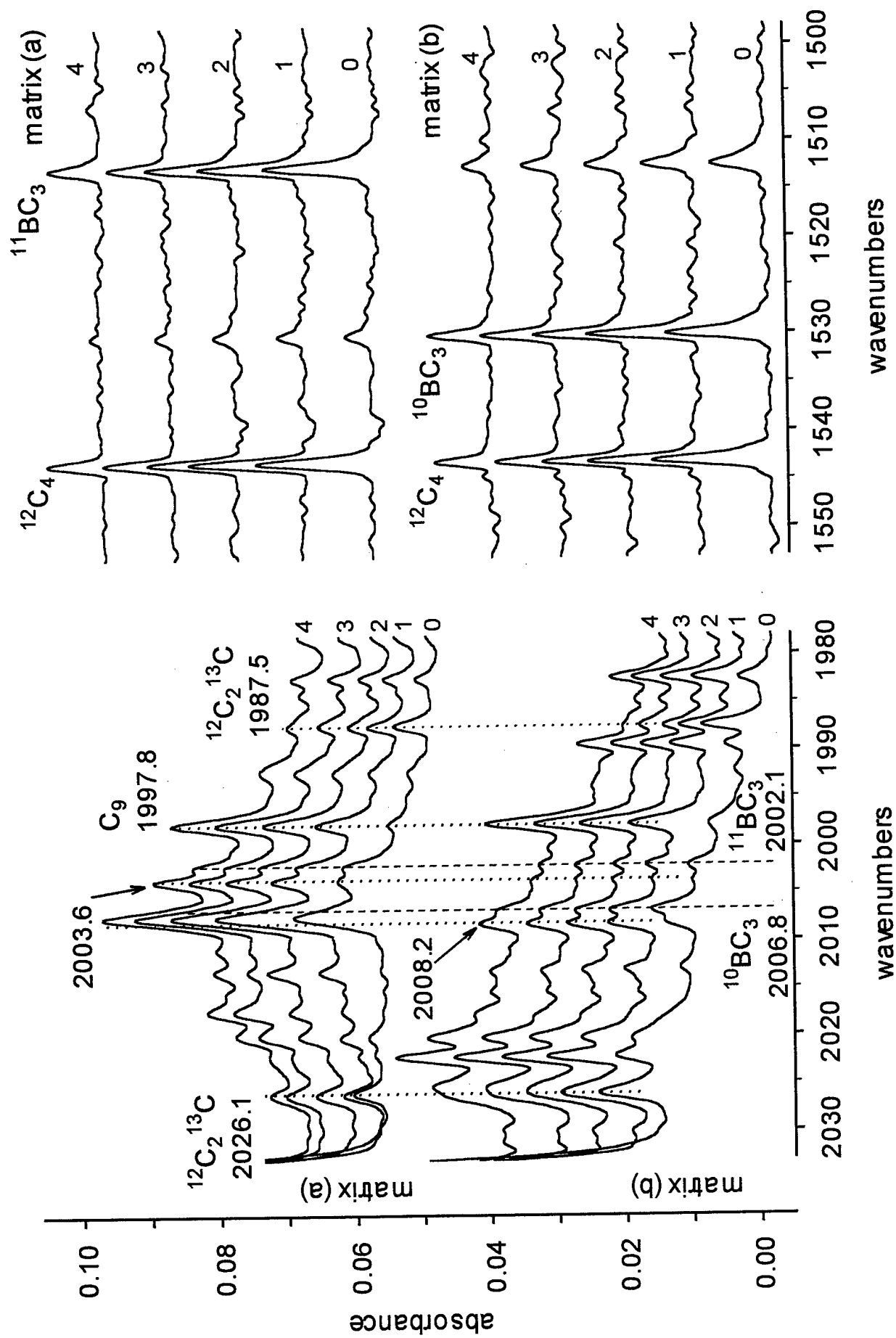Fig 1. Presilla-Marquez, et al.
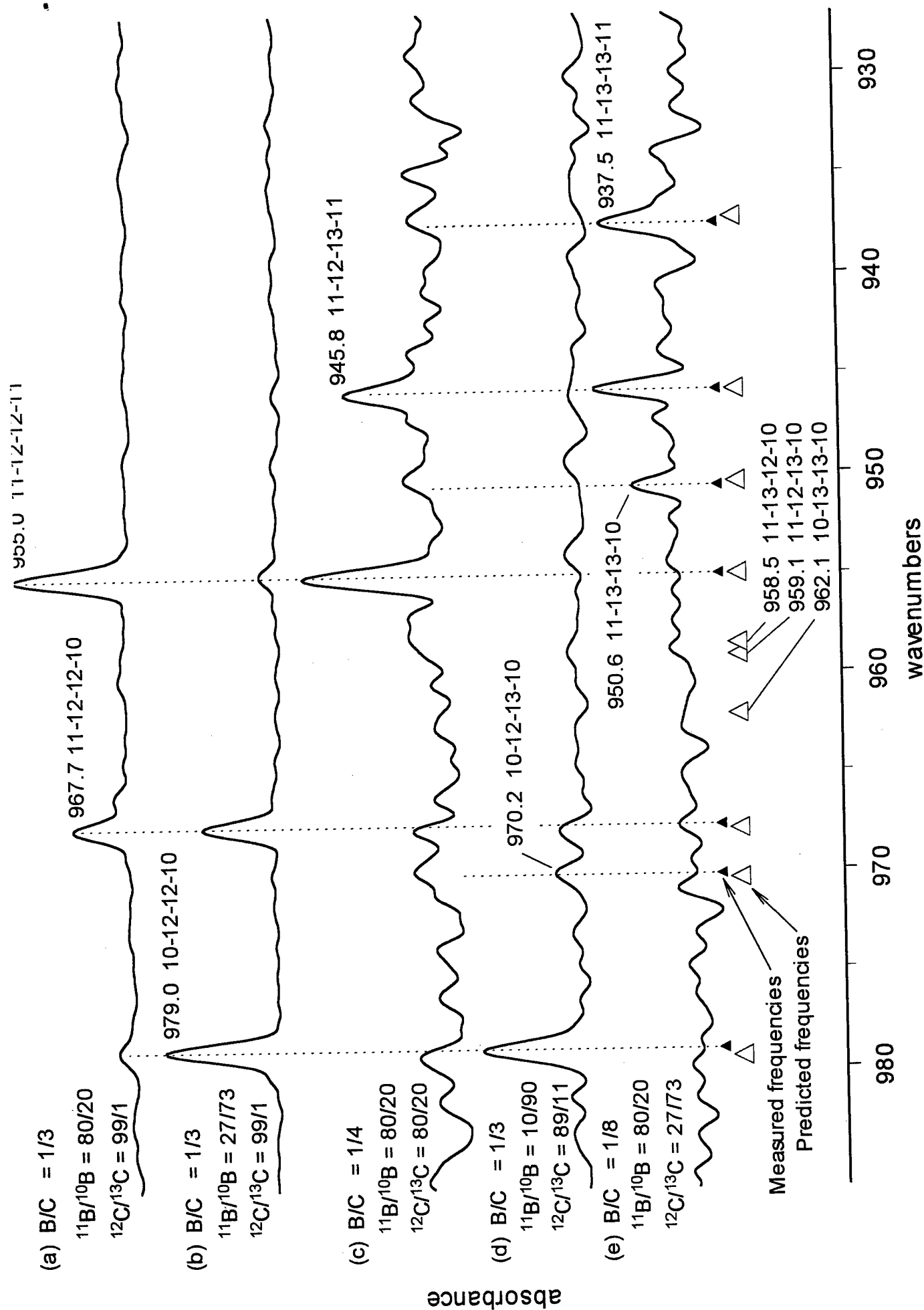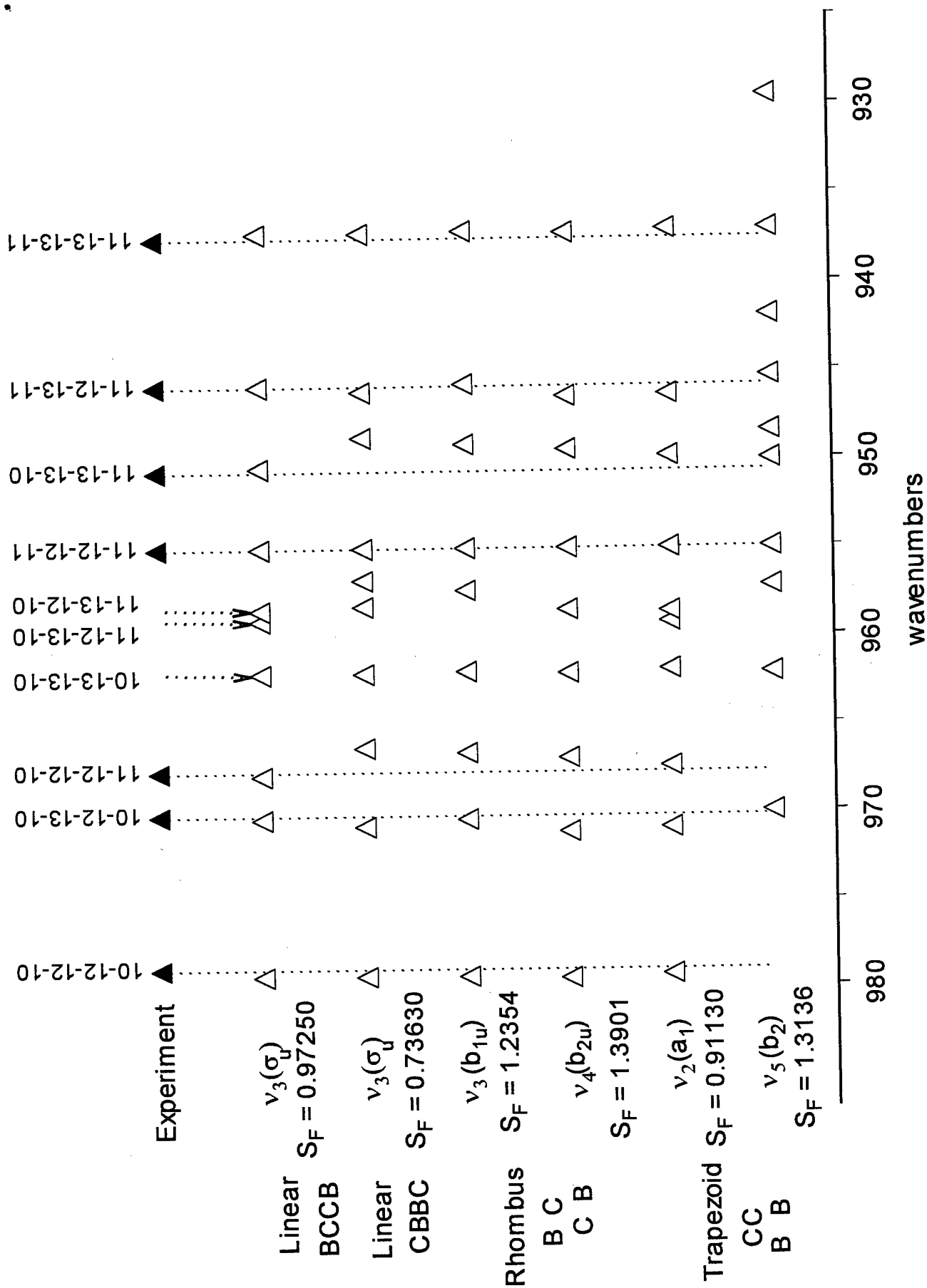
Fig. 2 Presilla-Marquez, et al.

Fig 3. Presilla-Marquez, et al.

Fig. 4. Presilla-Marquez, et al.